

## PATENT ABSTRACTS OF JAPAN

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(54) RUBBER COMPOSITION AND HEAVY-DUTY PNEUMATIC TIRE PRODUCED THEREFROM

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a rubber compsn. greatly improved in resistances to breaking and cutting and in low heat build-up properties and suitable for a tread base rubber by mixing and kneading a diene rubber with a carbon black, a compd. having a (substd.) acryloyloxy group, and silica under specified conditions.

SOLUTION: First, 100 pts.wt. diene rubber contg. at least 70wt.% natural rubber and/or synthetic polyisoprene rubber is mixed and kneaded with 20-60 pts.wt. carbon black having a nitrogen adsorption specific surface area of 70m<sup>2</sup>/g or higher and 0.05-6 pts.wt. compd. having at least two acryloyloxy or  $\alpha$ -alkyl- substd. acryloyloxy groups, then mixed and kneaded with 1-30 pts.wt. silica and 0.05-6 pts.wt. coupling agent, and finally mixed and kneaded with ingredients necessary for vulcanization. Thus obtd. compd. is vulcanized to give the objective compsn.

## LEGAL STATUS

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the rubber constituent used suitable for the base rubber of a tire tread in more detail, and the pneumatic tire for heavy loading using it about a silica compound constituent.

[0002]

[Description of the Prior Art] Generally, in the pneumatic tire for heavy loading used for a bus, a truck, etc., tread rubber excellent in abrasion resistance, low febrility, destruction-proof nature, etc. is required. Usually, since the pneumatic tire for heavy loading has large generation of heat inside the tread by run, tread rubber is made into a bilayer and the rubber constituent with a low febrility rubber constituent good to the cap rubber as outer layer rubber is used for the base rubber as inner layer rubber at abrasion resistance, chipping-proof nature, etc. On the other hand, conventionally, for the purpose which improves abrasion resistance, febrility, etc. of tread rubber, the rubber constituent of silica combination is proposed and much technology is indicated. For example, the rubber constituent which blended specific carbon black and a specific specific coupling agent with the silica is indicated by JP,1-92247,A.

[0003] However, in such conventional technology, although the appropriate effect was demonstrated about abrasion resistance or low febrility, it was difficult to obtain the rubber which was simultaneously excellent in destruction-proof nature, especially tear-resistance nature. Moreover, two or more -O-CO-CR=CH<sub>2</sub> combined with a carbon atom at JP,63-150339,A for the febrility-proof of diene system rubber, and the purpose which improves especially elevation of blowout temperature The rubber constituent which blended the compound which has a machine (R is hydrogen or an alkyl group) is proposed. However, in this technique, even if the thermal resistance of rubber was improved, the degree of hardness of rubber increased, and in order to fall, intensity had the fault that destruction-proof nature fell [ tear-resistance nature chipping-proof nature, etc. ] remarkably, especially when such a rubber constituent was used for the tread rubber of the pneumatic tire for heavy loading.

[0004]

[Means for Solving the Problem] That the above-mentioned trouble should be solved, wholeheartedly, as a result of examination, this invention person finds out that the above-mentioned trouble is solvable, and came to complete this invention by blending with natural rubber and/or a synthetic polyisoprene rubber the specific compound which has the compound which has a silica, an acryloyloxy machine, or two or more alpha-alkylation acryloyloxy machines, and devising kneading conditions to them. Namely, the 1st invention in this invention receives the diene system rubber 100 weight section which contains natural rubber and/or a synthetic polyisoprene rubber 70% of the weight or more. (1) Nitrogen adsorption specific surface area (N<sub>2</sub> SA) The carbon black 20 more than 70m<sup>2</sup>/g - 60 weight sections, (2) The compound 0.05 - 6 weight sections which have an acryloyloxy machine or two or more alpha-alkylation acryloyloxy machines, (3) It is offering the rubber constituent characterized by blending a silica 1 - 30 weight sections, and the (4) silane coupling agent 0.05 - 6 weight sections.

[0005] Moreover, the 2nd invention in this invention receives the diene system rubber 100 weight

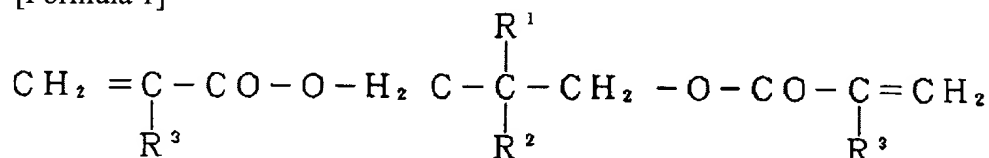
section which contains natural rubber and/or a synthetic polyisoprene rubber 70% of the weight or more. (1) Nitrogen adsorption specific surface area (N<sub>2</sub> SA) carries out 0.05-6 weight section combination of the compound which has 20 - 60 weight section, an acryloyloxy machine, or two or more alpha-alkylation acryloyloxy machines for the carbon black more than 70m<sup>2</sup>/g. After carrying out 1st kneading, it is offering the rubber constituent characterized by blending the (3) silica 1 - 30 weight sections, and the (4) coupling agent 0.05 - 6 weight sections, carrying out 2nd kneading further, and being obtained, and its manufacturing method. Furthermore, other invention in this invention is also offering the pneumatic tire for heavy loading which used the above-mentioned rubber constituent for tread base rubber, and its manufacturing method. Here, as for the curing temperature in a rubber constituent or tread base rubber, it is desirable that it is 150 degrees C or less.

[0006]

[Embodiments of the Invention] The rubber component in this invention is rubber which consists of natural rubber, and/or 70 - 100 % of the weight of synthetic polyisoprene rubbers and 30 - 0 % of the weight of other diene system synthetic rubber. as other diene system synthetic rubber -- cis-[ a styrene butadiene rubber and ] -- 1 and 4-polybutadiene rubbers, such mixture, etc. can be used When natural rubber and/or a synthetic polyisoprene rubber are less than 70 % of the weight, low febrility and destruction-proof nature fall. Moreover, as for the carbon black as a component (1), the thing of 70 - 170m<sup>2</sup> / g is used preferably more than nitrogen adsorption specific surface area of 70m<sup>2</sup> / g. the loadings of carbon black -- the above-mentioned rubber component 100 weight section -- receiving -- 20 - 60 weight section -- it is 25 - 50 weight section preferably Under in 20 weight sections, abrasion resistance falls, and if 60 weight sections are exceeded, low febrility will get worse. Moreover, as a compound which has the acryloyloxy machine or two or more alpha-alkylation acryloyloxy machines which are used as a component (2), although various kinds of things can be mentioned, it is preferably expressed with the following general formula.

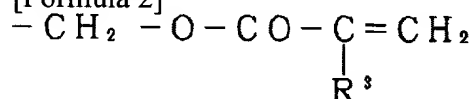
[0007]

[Formula 1]



[0008] (The inside of a formula, R<sup>1</sup>, and R<sup>2</sup> are hydrogen, the alkyl group of carbon numbers 1-20, or [0009], respectively.)

[Formula 2]



[0010] A basis is shown and it is R<sup>3</sup>. They are hydrogen or the alkyl group (especially preferably methyl group) of carbon numbers 1-5. two or more R<sup>3</sup> [ however, ] Even if respectively the same, you may differ.

[0011] Still more preferably, the compound of the component (2) by the above-mentioned general formula is a compound which has an acryloyloxy machine or three or more alpha-alkylation acryloyloxy machines, and trimethylolpropane triacrylate and its trimethylolpropanetrimethacrylate are especially desirable. In addition to this 1 and 3-butylene-glycol diacrylate; 1,5-pentanediol diacrylate; Neopentyl-glycol-diacrylate; 1 and 6-hexanediol diacrylate; Diethylene-glycol-diacrylate; Triethylene-glycol-diacrylate; Tetraethylene-glycol-diacrylate; Polyethylene-glycol diacrylate; Polypropylene-glycol diacrylate; pentaerythritol thoria chestnut rate; -- tetramethylolmethane tetraacrylate; -- a dipentaerythritol hexa / pentaacrylate; -- dipropylene-glycol dimethacrylate; -- trimethylolthane trimethacrylate etc. is mentioned the loadings of the above-mentioned component (2) used by this

invention -- the rubber 100 weight section -- receiving -- 0.05 - 6 weight section -- it is 0.2 - 2 weight section preferably Under in the 0.05 weight section, the synergistic effect with a silica is not acquired, but if 6 weight sections are exceeded, destruction-proof nature, such as tear-resistance nature and chipping-proof nature, will fall.

[0012] Moreover, especially the silica as a component (3) used by this invention is not restricted, and the well-known thing from the former can be widely used for it, for example, the silicic acid anhydride by dry process, the water silicic acid by the wet method, a synthetic silicic acid, etc. are mentioned. the loadings of a silica -- the above-mentioned rubber component 100 weight section -- receiving -- 1 - 30 weight section -- it is 5 - 20 weight section preferably Under in 1 weight section, when a blending effect is not obtained but 30 weight sections are exceeded, low febrility gets worse. Furthermore, although the coupling agent as a component (4) used by this invention is a binder of a silica and rubber and it is not restricted especially, a silane coupling agent is used preferably. the loadings of a coupling agent -- the rubber 100 weight section -- receiving -- 0.05 - 6 weight section -- it is 0.5 - 2 weight section preferably There is no blending effect, by the case where 6 weight sections are exceeded, a rubber degree of hardness increases and chipping-proof nature and tear-resistance nature fall under at the 0.05 weight section.

[0013] In order to obtain the rubber constituent in this invention, in the kneading process, it is effective to dissociate, and to blend and distribute the compound which carries out the acryloyloxy machine as a component (2) or two or more alpha-alkylation acryloyloxy machines, and the silica as a component (3). If the reason blends the compound of a component (2), and the silica of a component (3) simultaneously, the compound of a component (2) will be considered because the blending effect is reduced by adsorbing a silica. That is, in the 1st phase of rubber kneading at the time of combination, in the 2nd phase, a silica and a coupling agent are blended, mixed distribution is carried out, and the rubber constituent in this invention is obtained by blending vulcanization related compounding agents, such as a vulcanizing agent and a vulcanization accelerator, in the 3rd phase, after blending the compound as the aforementioned component (2) with carbon black first and carrying out mixed distribution. In addition, process oil, a zinc white, stearin acid, an antioxidant, etc. are suitably blended with the rubber constituent of this invention as other compounding agents. The above-mentioned kneading is performed by usual kneading equipment, for example, a roll, a Banbury mixer, the kneader, etc. Furthermore, the curing temperature of the rubber constituent in this invention has desirable 150 degrees C or less. It is because a rubber degree of hardness becomes large and destruction-proof nature falls, in vulcanizing exceeding 150 degrees C.

[0014] Next, application to the pneumatic tire of this invention using the above-mentioned rubber constituent is explained. Especially the rubber constituent by this invention is suitably used as tread base rubber of the pneumatic tire for heavy loading. Here, as for the volume ratio of cap rubber and base rubber, it is [ a tread ] desirable that it is the range of 90 / 10 - 10/90. When cap rubber exceeds 90 part by volumes, the maintenance of low febrility of a tire is difficult, and cap rubber is because abrasion resistance falls in less than ten part by volumes. Moreover, it is desirable that especially face to manufacture the above-mentioned tire and the curing temperature of the tread base section makes it 120-150 degrees C 150 degrees C or less. Below 150 degrees C, since the reactivity of the end double bond and sulfur with which the compound of a component (2) has vulcanization \*\*\*\* is comparatively small The unreacted compound remains after vulcanization. that also unexpectedly It is because a big effect is demonstrated to advance crosslinking reaction with rubber very gradually by the exoergic operation at the time of a tire run, and suppress exoergic softening of the rubber in the tire run last stage, and setting and the fall of low febrility.

[0015]

[Example] Hereafter, although an example and the example of comparison explain this invention concretely, this invention is not restrained at all by these.

The compounding agent was kneaded according to the content of combination and sequence examples 1-4 and the example 1 of comparison - given in 6 1st table, and the rubber constituent was prepared. Next, this rubber constituent is used for tread base rubber, and it vulcanizes by the curing temperature

shown in the 1st table, and is 10.00R20. The tire for 14PR right ways was produced, and it considered as the sample offering tire. In addition, the volume ratio of the cap rubber of a tread and base rubber was 50/50. The evaluation method equipped 10t truck with the above-mentioned sample offering tire, and performed it by the following method after 100,000km run by the load of JIS regular internal pressure. [0016] (1) At the time of the modulus and fracture of rubber, from the tire after an elongation run, a part of tread base rubber was started, JIS#3 sample was produced, and this was measured with the Instron hauling testing machine.

(2) The state of a pattern block of destruction-proof nature tread both ends was observed.

(3) The channel depth in the state where the base rubber after wear-resistant cap rubber \*\*\*\* appeared in the road surface was observed.

(4) Counting of the number of cut-proof nature belt attainment cuts was carried out.

(5) The exoergic temperature in the boundary section of a low febrility belt and tread rubber was measured. 3 stage evaluations of O (it excels), O (it is good), and x (it is inferior) showed each property as a tire performance respectively. A result is shown in the 1st table.

[0017]

[Table 1]

第1表

トレッドベースゴムの配合 (配合単位は重量部)			実施例			
			1	2	3	4
混練の段階	第1	天然ゴム	100	100	100	100
		カーボンブラック	30	30	30	30
		トリメチロールポロブタジエン	1.0	1.0	1.0	--
		トリメチロールポロブタジエン	--	--	--	1.0
	第2	シリカ	10	10	5	10
		カップリング剤	1.0	0.5	0.5	1.0
	第3	加硫促進剤	1	1	1	1
		硫黄	1	1	1	1
	ベースゴムの加硫温度 (°C)		145	145	145	145
	タイヤ性能	50%モデュラス (MPa)	1.15	1.05	0.97	1.18
		300%モデュラス (MPa)	11.5	10.9	10.0	11.7
		破断時伸び (%)	576	601	595	562
		耐破壊性	◎	◎	◎	◎
		耐摩耗性	◎	◎	○	◎
		耐カット性	◎	◎	○	◎
		低発熱性	◎	○	○	◎

[0018]

[Table 2]

第1表 (つづき)

トレッドベースゴムの配合 (配合単位は重量部)			比較例					
			1	2	3	4	5	6
混練の段階	第1	天然ゴム	100	100	100	100	100	100
		カーボンブラック	30	30	30	30	30	40
		トリメチロールプロパントリアクリレート	1.0	--	10.0	1.0	--	--
		トリメチロールプロパントリメタクリレート	--	--	--	--	--	--
	第2	シリカ	--	--	10	10	10	--
		カップリング剤	--	--	1.0	1.0	1.0	--
	第3	加硫促進剤	1	1	1	1	1	1
		硫黄	1	1	1	1	1	1
	ベースゴムの加硫温度 (°C)		145	145	145	160	145	145
タイヤ性能	50 %モデュラス (MPa)		0.82	0.79	1.85	1.31	1.14	1.03
	300 %モデュラス (MPa)		8.99	8.52	20.0	14.2	11.2	12.0
	破断時伸び (%)		480	605	313	420	580	540
	耐破壊性		×	◎	×	×	◎	○
	耐摩耗性		×	×	◎	◎	◎	◎
	耐カット性		○	×	◎	◎	◎	◎
	低発熱性		◎	×	◎	×	×	×

[0019] notes 1) In the 1st phase of kneading, the stearin acid 2 weight section, the zinc white 4 weight section, and the antioxidant 1 weight section were used as compounding agents other than an upper \*\* publication.

notes 2) The nitrogen adsorption specific surface area (N2 SA) of the carbon black used with upper \*\* is 120m<sup>2</sup>/g.

[0020] The above result shows the following thing. Although it turns out as a component (2) that destruction-proof nature is improved without all reducing other performances although an example 4 is the case where trimethylolpropanetrimethacrylate is used when trimethylolpropane triacrylate is used, especially the examples 1 and 4 excel [ examples / 1-3 ] in destruction-proof nature, abrasion resistance, cut-proof nature, and all the performances of low febrility. On the other hand, in any case, abrasion resistance is extremely inferior although the example 1 of comparison is the case where a silica is not used together although trimethylolpropane triacrylate is blended, and the example 2 of comparison is the case where neither the compound as a component (2) nor a silica is blended. Although the example 3 of comparison is the case where it carries out like an example 1, except having increased the quantity of trimethylolpropane triacrylate, especially since there are loadings of a component (2) out of range [ this invention ], it is inferior in destruction-proof nature. Moreover, although the example 4 of comparison is the same combination as an example 1, it is the case where the curing temperature of tire base rubber is over 150 degrees C, and is inferior in destruction-proof nature and low febrility. Since the example 5 of comparison blends only a silica and a component (2) is not included, softening by generation of heat of rubber, and setting and the fall of low febrility are large in the tire run last stage. Furthermore, although the example 6 of comparison increases only the quantity of carbon black in the example 2 of comparison for wear-resistant improvement, it becomes an increase of generation of heat simply, and low febrility is getting worse.

[0021] Furthermore, although drawing 1 is the stress at the time of performing the hauling examination

of the base rubber extracted from the tire after 100,000km run about an example 1, the above-mentioned example 3 of comparison, and the above-mentioned example 6 of comparison - a distortion curve, it turns out that the example 1 by this invention is excellent in all low febrility, the cut-proof nature, and destructive-proof properties. Next, about some tires of the above-mentioned example and the example of comparison, mileage was changed and the same evaluation as the above was performed. The result is shown in drawing 2 - drawing 3 . Drawing 2 is drawing showing the relation of the 300% modulus and mileage of tread base rubber about the tire of an example 1 and the example 5 of comparison.

Consequently, the example 1 by this invention of change of 300% modulus by run is small. Drawing 3 is drawing showing the relation between elongation (at the time of fracture distortion), and mileage about the tire of an example 1 and the examples 2 and 5 of comparison at the time of fracture of each tread base rubber. Consequently, the example 1 by this invention of change of elongation is small at the time of fracture by run.

[0022]

[Effect of the Invention] According to this invention, the rubber constituent with which destruction-proof nature, cut-proof nature, low febrility, etc. were improved greatly is offered. Moreover, the pneumatic tire for heavy loading which used this constituent for tread base rubber is excellent in endurance, and can maintain good appearance also in the tire life last stage after a long-term run.

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[Translation done.]



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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to the rubber constituent for tire treads of low febrility.

[0002]

[Description of the Prior Art] Forming the rubber constituent for tire treads into low generation of heat conventionally using the chemical of a hydrazide system etc. is already known. However, if the conventional low generation-of-heat-ized agent is used, the viscosity of the rubber constituent for tire treads will increase sharply, and there is a trouble of spoiling workability by YAKE etc. Moreover, when softeners, such as aroma oil, are used for the rubber constituent for tire treads for a workability improvement, there is a trouble that a destructive property, especially the destructive property and heat generation characteristic at the time of an elevated temperature are spoiled.

[0003]

[Problem(s) to be Solved by the Invention] The purpose of this invention is to offer the rubber constituent for tire treads which has improved sharply workability which is the problems of a low generation-of-heat-ized agent, such as a viscosity steep rise and YAKE, maintaining the low febrility of a low generation-of-heat-ized agent.

[0004]

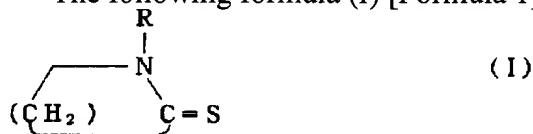
[Means for Solving the Problem] When this invention person etc. blended with the low febrility improvement agent combining specific unsaturated fatty acid to at least one sort of rubber components chosen from the group which consists of natural rubber and diene system synthetic rubber as a result of inquiring wholeheartedly, in order to solve the aforementioned technical problem, he does the knowledge of demonstrating the outstanding workability, and came to complete this invention, maintaining the low febrility improvement effect. That is, the rubber constituent for tire treads of this invention is characterized by containing a following (a) - (c) component to at least one sort of rubber component 100 weight sections chosen from the group which consists of natural rubber and diene system synthetic rubber.

(\*\*) Reinforcement nature bulking agent 20 - 100 weight section (b) Low febrility improvement agent 0.1- 10 weight sections (c) At least 1 set of the double bond between [ of two pieces ] carbon which has a conjugate relation is included in a molecule. They are two pieces about the double bond between carbon in the molecule which contains conjugate dienoic acid 10% of the weight or more. Organic unsaturated fatty acid included above 0.1- 20 weight sections. [0005] Hereafter, the content of this invention is explained. One sort of rubber chosen from at least one sort chosen from the group which consists of natural rubber and diene system synthetic rubber as rubber used for the rubber constituent for tire treads of this invention, for example, natural rubber, butadiene rubber, synthetic polyisoprene rubber, the styrene butadiene rubber, etc. or these copolymerization objects, and mixture are mentioned. [0006] The reinforcement nature bulking agent used by this invention means the tensile strength of rubber, a tearing strength, and the bulking agent that increases at least one of the abrasion resistances. As such a reinforcement nature bulking agent, carbon black, such as SAF, ISAF, and HAF, or a silica is

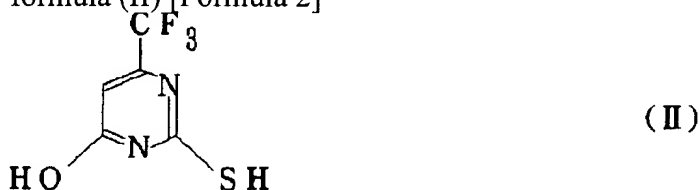
mentioned, for example. the loadings of a reinforcing filler -- the rubber component 100 weight section -- receiving -- the 20 - 100 weight section -- desirable -- 30 - 90 weight section -- it is 35 - 80 weight section still more preferably 300% tensile stress and hardness fall that the loadings of a reinforcing filler are under 20 weight sections, it is not desirable, and if the 100 weight sections are exceeded, tensile strength and elongation fall and are not desirable.

[0007] As a low febrility improvement agent used by this invention, the compound of \*\* - \*\* can be mentioned below, for example.

\*\* The following formula (I) [Formula 1]

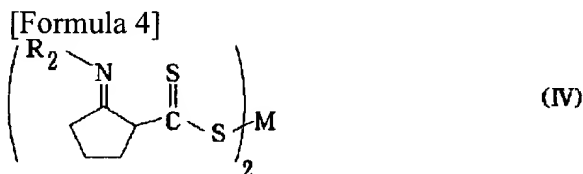
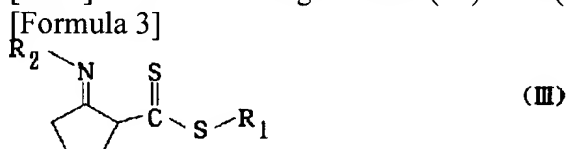


It comes out and, specifically, gamma-thio butyrolactam, omega-CHIORAU phosphorus lactam, an N-methyl-gamma-thio butyrolactam, etc. are mentioned by the lactams expressed. [0008] \*\* The following formula (II) [Formula 2]



4-trifluoromethyl-2-thiouracil come out of and expressed.

[0009] \*\* the following formula (III) -- or (IV) --



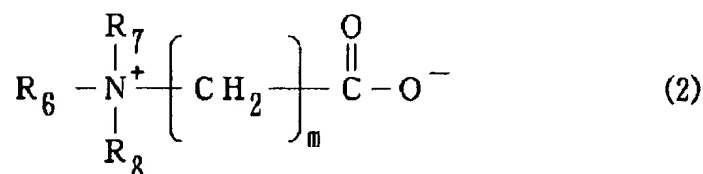
In R1 in [a formula (III) or (IV)], a hydrogen atom, the alkyl group of carbon numbers 1-6 or 2-ARUKIRUIMINO cyclopentane dithio carbonyl group, and R2 express the alkyl group of carbon numbers 1-6, or the cycloalkyl machine of 5-6, and M expresses alkaline earth metal, copper, or nickel. ] It comes out and, specifically, a 2-methylimino pentane dithiocarboxylic-acid, screw (2-methylimino cyclopentyl thiocarbonyl) disulfide, 2-methylimino cyclopentane dithiocarboxylic-acid methyl, 2-methylimino cyclopentane dithiocarboxylic-acid zinc, 2-cyclohexyl imino cyclopentane dithiocarboxylic-acid, and 2-methylimino cyclopentane dithiocarboxylic-acid-n-hexyl, 2-methylimino cyclopentane dithiocarboxylic-acid nickel, etc. are mentioned by the ring compound expressed.

[0010] \*\* 2, 5-dimercapto - The mixture of the compound expressed with 1, 3, and 4-thiadiazole independent and following formula (1) - (9) is mentioned.

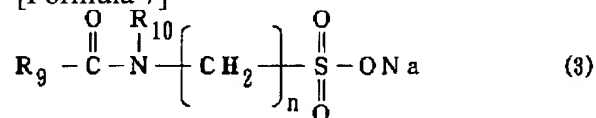
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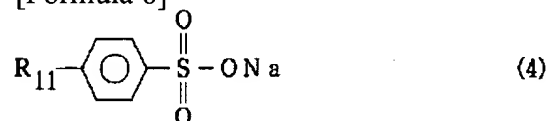
[Formula 6]



[Formula 7]



[Formula 8]



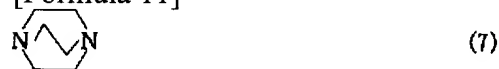
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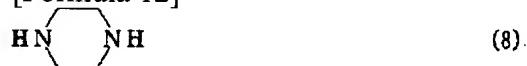
[Formula 10]



[Formula 11]



[Formula 12]



[Formula 13]



R3, R6, R9, and R11 in [formula (1) - (9)] The alkyl group and allyl group of carbon numbers 8-18, for R4, R5, R7, R8, and R10, as for an allyl group, a cyclohexyl machine, and R16, the alkyl group of carbon numbers 1-6, and R17 and R18 are [ the alkyl group of carbon numbers 1-2 and R15 ] the alkyl group of carbon numbers 8-18, a benzyl, and a hydrogen atom, and m and n show the integer of 1-3, respectively ]

[0011] \*\* The following formula (VI)

[Formula 14]



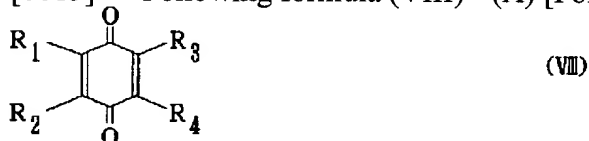
(-- as for the inside R1 of a formula, and/or R2, a hydrogen atom, a methyl group, an ethyl group, and R4 show a hydrogen atom and the alkyl group of carbon numbers 1-4, and R3 shows a hydrogen atom and the alkyl group of carbon numbers 1-6 the dithio uracil compound expressed with) -- specifically, a dithio uracil, a 3-n-butyl dithio uracil, a 1-n-butyl dithio uracil, 5-ethyl dithio uracil, a 4-n-hexyl dithio uracil,

[0012] \*\* The following formula (VII) [Formula 15]



(R1, R2, R3, and R4 in a formula are a hydrogen atom, a chlorine atom, an alkyl group, an alkoxy group, a cyano group, and a phenyl group separately.) P-benzoquinone, 2, a 5-dimethyl-P-benzoquinone, 2, a 5-G t-butyl-P-benzoquinone, 2, a 5-dichloro-P-benzoquinone, 2, 3-dichloro -5, a 6-dicyano-P-benzoquinone, 2, a 6-G t-butyl-P-benzoquinone, 2, a 6-dichloro-P-benzoquinone, 2, a 6-dimethoxy-P-benzoquinone, a 2-methyl-P-benzoquinone, a 2-t-butyl-P-benzoquinone, a tetracyano-P-benzoquinone, a phenyl-P-benzoquinone, etc. can be mentioned.

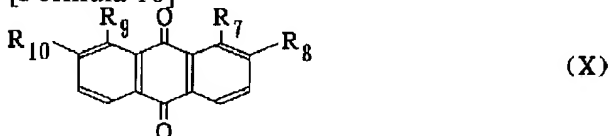
[0013] \*\* Following formula (VIII) - (X) [Formula 16]



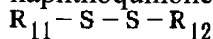
[Formula 17]



[Formula 18]



At least one sort of compounds which came out and were chosen from the benzoquinone expressed, the naphthoquinone, and the anthraquinone compound, and following formula (10) - (11) [Formula 19]



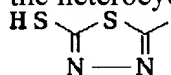
[Formula 20]



The combination of at least one sort of compounds which came out and were chosen from the compound expressed is mentioned.

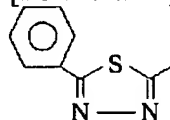
[0014] Specifically as benzoquinones (VIII) P-benzoquinone, 2, a 5-dimethyl-P-benzoquinone, 2, a 5-G t-butyl-P-benzoquinone, 2, a 5-dichloro-P-benzoquinone, 2, 3-dichloro -5, a 6-dicyano-P-benzoquinone, 2, a 6-G t-butyl-P-benzoquinone, 2, a 6-dichloro-P-benzoquinone, 2, a 6-dimethoxy-P-benzoquinone, a 2-methyl-P-benzoquinone, a 2-t-butyl-P-benzoquinone, a tetracyano-P-benzoquinone, a phenyl-P-benzoquinone, etc. can be mentioned. As naphthoquinones (IX), it is 1, 4-naphthoquinone, 1,2-naphthoquinone, a 2, 3-dichloro-1, 4-naphthoquinone, the 2-methyl -1, 4-naphthoquinone, and hydroxy.

- 1, 4-naphthoquinone, dihydroxy -1, 4-naphthoquinone, etc. can be mentioned. As anthraquinone (X), they are anthraquinone, hydroxy anthraquinone, dihydroxyanthraquinone, an aminoanthraquinone, diamino anthraquinone, etc. The concrete targets of the compound shown by the formula (10) are a dibenzothiazyl sulfide, 5, and 5'-dithio screw (1, 3, 4-thiadiazole-2-thiol), a tetraethylthiuram disulfide, tetrabutylthiuram disulfide, tetramethylthiuramdisulfide, TETORAISO octyl thiuram disulfide, etc. The example of the compound shown by the formula (11) is 2 and 5-dimercapto. - They are 1, 3, 4-thiadiazole, a mercapto benzimidazole, a mercaptobenzothiazole, a mercapto oxazole, 2-mercaptoethanol, 3-mercapto-2-propanol, 3-mercaptopropionic acid, 2-mercapto ethyl ether, 2-mercapto ethyl sulfide, a 2-mercapto-5-nitroglycerine imidazole, the 3-mercapto -1, 2-propanediol, 2-mercapto pyridine, a mercapto SUKUSHIN acid, mercapto thiazoline, [0015] [-- R1-R10 are a hydrogen atom, a chlorine atom, the alkyl group of carbon numbers 1-4, an alkoxy group, a cyano group, and a phenyl group among above-mentioned formula (VIII) - (X) and (10) - (11), and R11-R13 express the alkyl group of the carbon numbers 1-4 including a hydrogen atom, a hydroxyl, ester combination, ether linkage, and thioether combination, or the functional group which has the heterocycle shown by following formula (12) - (20) [Formula 21]



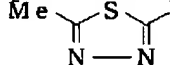
(12)

[Formula 22]



(13)

[Formula 23]



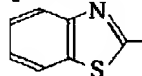
(14)

[Formula 24]



(15)

[Formula 25]



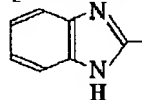
(16)

[Formula 26]



(17)

[Formula 27]



(18)

[Formula 28]



(19)

[Formula 29]



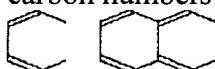
(20)

[0016] \*\* The mercapto compound expressed with the following formula (XI) is mentioned.

[Formula 30]



(Respectively, independently, the inside R1 and R2 of a formula is a hydrogen atom, the alkyl group of carbon numbers 1-3, or R1 to R2, and is the following chemical formula.) [Formula 31]



Or you may form a carbon number 3 or the alkylene ring of 4. [0017] Furthermore, as a low febrility improvement agent used by this invention, things, such as what [ not only ] was shown above but a hydrazide system, a thiadiazole system, etc., are mentioned. It is required to the rubber component 100 weight section 0.1 - 10 weight section and to use the loadings of a low febrility improvement agent in the range of 0.5 - 8 weight section preferably. The low febrility of a rubber constituent does not appear that the loadings of a low febrility improvement agent are under the 0.1 weight section, and it is not desirable, and if 10 weight sections are exceeded, the workability of an unvulcanized rubber is reduced remarkably and it is not desirable.

[0018] The organic unsaturated fatty acid used by this invention consists of organic unsaturated fatty acid including two or more double bonds between carbon in the molecule which contains the conjugated-diene acid which contains in a molecule at least 1 set of the double bond between [ of two pieces ] carbon which has a conjugate relation 10% of the weight or more. In the organic unsaturated fatty acid used by this invention, "conjugate dienoic acid" shows an organic unsaturation monocarboxylic acid including at least 1 set of double bond between [ of two pieces ] carbon which has a conjugate relation in the molecule, and although the thing of a lot is desirable, it may have 2 or more sets of double bonds between carbon which have a conjugate relation. the organic unsaturated fatty acid (only henceforth organic unsaturated fatty acid) which includes two or more double bonds between carbon in the molecule which contains the aforementioned conjugate dienoic acid 10% of the weight or more is natural -- although a conjugated-diene acid is included, and the other organic unsaturated fatty acid includes two or more double bonds between carbon, the points that there are no they in a conjugate relation mutually differ

[0019] 10 % of the weight or more may be required for the content in the organic unsaturated fatty acid of a conjugated-diene acid, its 25 % of the weight or more may be desirable, and all of 100 % of the weight, i.e., organic unsaturated fatty acid, may be conjugate dienoic acid. Less than 10 % of the weight is not enough as the effect as opposed to abrasion resistance in the content of a conjugated-diene acid. Moreover, the effect as opposed to [ that the content of a conjugated-diene acid is 25 % of the weight or more ] abrasion resistance improves further.

[0020] As a conjugated-diene acid, 2, 4-pentadiene acid, 2, 4-hexadiene acid, 2, 4-deca dienoic acid, 2, 4-dodeca dienoic acid, 9, 11-octadecadienoic acid, alpha-Herriot stearin acid, 9, 11 and 13, 15-OKUTA deca tetraenoic acid, 9 and 11, 13-octadecatrienoic acid, etc. are mentioned, for example.

[0021] A dehydrated-castor-oil fatty acid is mentioned as a desirable example of the organic unsaturated fatty acid used by this invention. This dehydrated-castor-oil fatty acid carries out dehydration of the castor oil, and is obtained. The content of a conjugated-diene acid can be changed by the method of dehydration, for example, 35 % of the weight and 60% of the weight of a thing is obtained. In the case of this dehydrated-castor-oil fatty acid, as a conjugated-diene acid, 9 and 11-octadecadienoic acid are

main, and disconjugation octadecadienoic acid is mainly contained in other organic unsaturated fatty acid, in addition linolic acid, the Reno Laing acid, etc. are mentioned. Moreover, you may use together the fatty acids currently used from the former which is represented with this invention by stearin acid in addition to a dehydrated-castor-oil fatty acid.

[0022] As for the organic unsaturated fatty acid used by this invention, it is desirable among [ all ] unsaturated fatty acid to contain 10-22, and the unsaturated fatty acid that has the long-chain alkyl group of 12-22 preferably for the carbon number 75% or more. The effect as opposed to [ that carbon numbers are 10-22 ] destruction-proof nature improves further. Moreover, it is desirable that the degree of unsaturation of all unsaturated fatty acid is 130 or more in the iodine number. The effect as opposed to [ that the iodine number is 130 or more ] the elastic modulus of rubber improves further.

[0023] It is required to the rubber component 100 weight section 0.1 - 20 weight section and to carry out 0.5-8 weight section combination of the loadings of the organic unsaturated fatty acid used by this invention preferably. In under the 0.1 weight section, when the loadings of organic unsaturated fatty acid blend with improvement of workability exceeding \*\*\*\*\* and 20 weight sections, they cause decline in the rate of rubber elasticity and are not desirable.

[0024] In this invention, besides the aforementioned rubber component, a low febrility improvement agent, and an organic unsaturated fatty acid agent, it is usually used as a compounding for rubber, for example, a process oil, a softener, an antioxidant, a vulcanization accelerator, a vulcanization promotion assistant, a zinc white, sulfur, a foaming agent, etc. can be blended suitably. moreover, the rubber component 100 weight section -- receiving -- a softener besides the above-mentioned organic unsaturated fatty acid -- 10 weight sections -- you may blend below 6 weight sections preferably

[0025]

[Example] Hereafter, although an example and the example of comparison explain this invention still in detail, this invention is not limited to these examples at all.

[0026] (Examples 1-4, examples 1-7 of comparison) The rubber constituent for tire treads was prepared according to combination prescription of the following table 1. The Mooney viscosity (ML 1+4) of this rubber constituent, the degree of ultimate elongation of the rubber after vulcanization of this rubber constituent (Eb), the elastic modulus at the time of 300% extension, 25 degrees C 2% The result which measured tandelta is shown in the following table 1. The above-mentioned Mooney viscosity (ML 1+4), the degree of ultimate elongation (Eb), the elastic modulus (Mod) at the time of 300% extension, 25 degrees C 2% tandelta was measured by the following method.

[0027] (1) Mooney viscosity (ML 1+4)

It measured at 130 degrees C using the Shimadzu Mooney viscometer. The examining method is JIS. It carried out based on K6300, ML 1+4 (MUNI value after a 1-minute preheating and 4-minute operation) was calculated, and it expressed as the index (Index).

(2) The elastic modulus (Mod) and Mooney viscosity JIS at the time of the degree of ultimate elongation of vulcanized rubber (Eb), and 300% extension K It evaluated according to 6301.

(3) 25 degrees C 2% Using the tandelta Iwamoto factory viscoelasticity spectrometer, it was distorted 2% and 25 degrees C [ per sample with a length / of 20mm / x width-of-face / of 5mm / x thickness of 2mm ] ROSUTANJIENTO tandelta was measured. In addition, the example 1 of comparison is considered as control, and they are Mooney viscosity (ML 1+4), the degree of ultimate elongation (Eb), an elastic modulus (Mod) at the time of 300% extension, and 25 degrees C. 2% tandelta was expressed with the index set to 100.

[0028]

[Table 1]

		比較例 1	比較例 2	比較例 3	実施例 1	比較例 4	比較例 5	比較例 6	実施例 2	実施例 3	実施例 4	比較例 7
R S S # 3		100	100	100	100	100	100	100	100	100	100	100
ノクイザ-SK *1		0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
カーボンブラック (HAF)		40	40	40	40	40	40	40	40	40	40	40
Z n O		4	4	4	4	4	4	4	4	4	4	4
ステアリン酸		2	2	2	2	2	2	2	2	2	2	2
老防F810NA *2		1	1	1	1	1	1	1	1	1	1	1
D M *3		0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
N S *4		0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
硫 黄		2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
I D H *5		0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
アロマオイル			3			15			3			
D C O - F A *6					3	3	0.05	25	5	1	17	
オレイン酸				3								
リノール酸												3
指 数	コパノゾ ML <sub>1+4</sub>	100	95	97	94	86	100	84	88	96	86	96
	E b	100	106	105	105	115	100	103	107	101	109	105
	300% Mod	100	93	97	100	85	100	98	100	101	100	98
	25℃ 2% tan δ	100	104	100	100	110	100	103	100	100	104	100

\*1 シャク解剤 (大内新興(株)の商品名)

\*2 N-フェニル-N'-イソプロピル-p-フェニレンジアミン (IPPD)

\*3 ジベンゾチアルジサルファイドの商品名

\*4 N-ヒューブチル-2-ベンゾチアゾリルスルフェンアミド

\*5 イソフタル酸ジヒドラジド

\*6 共役ジエン酸含量35重量%の脱水ひまし油脂肪酸

[0029] The following thing became clear from the result of Table 1. It compares with the examples 1-7 of comparison which are the rubber constituents for tire treads contained in the range of this invention, and are not included in the range of this invention, and examples 1-4 are Mooney viscosity (ML 1+4), the degree of ultimate elongation (Eb), an elastic modulus (Mod) at the time of 300% extension, and 25 degrees C. 2% It turns out that tandelta is improving remarkably.

[0030]

[Effect of the Invention] According to this invention, the rubber constituent for tire treads which demonstrates the outstanding workability is offered, maintaining the low febrility improvement effect.

[Translation done.]